Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2017.21538

94 (2017) 189–197
October

The modelling of arsenic removal from water by deep eutectic solvents functionalized CNTs: Artificial neural network (ANN) approach

Seef Saadi Fiyadh[a], Mohammed Abdulhakim AlSaadi[a,b,*], Mohamed Khalid AlOmar[b,c], Sabah Saadi Fayaed[d], Sharifa Bee[a], Ahmed El-Shafie[c,**]

[a]*Nanotechnology & Catalysis Research Centre (NANOCAT), IPS Building, University of Malaya, 50603 Kuala Lumpur, Malaysia, email: saadisaif3@gmail.com (S. Fiyadh), Tel. +60163630693, Fax +60 3 7967 5311, email: mdsd68j@gmail.com (M. AlSaadi), sharifahbee@um.edu.my (S. Bee)*
[b]*University of Malaya Centre for Ionic Liquids, University Malaya, Kuala Lumpur 50603, Malaysia*
[c]*Department of Civil Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia, email: mohd.alomar@yahoo.com (M.K. AlOmar), Tel. +60122003857, email: elshafie@um.edu.my (A. Elshafie)*
[d]*Civil Engineering Department, Faculty of Engineering, Komar University of Science and Technology, Sulaymaniyah, Iraq, email: sabah.saadi@komar.edu.iq (S.S. Fayaed)*

Received 8 April 2017; Accepted 5 October 2017

ABSTRACT

In this work, novel adsorbent was developed by using deep eutectic solvent system as functionalization agent of carbon nanotubes for the removal of arsenic ions from water. Artificial neural network (ANN) approach was used to predict arsenic removal from water. The developed adsorbent was characterized using Raman spectroscopy, Zeta potential and FTIR. The experimental work was designed to study adsorption process parameters and they were initial concentration of arsenic, adsorbent dosage, pH and contact time. After using three models to identify the suitable kinetic model with different pH values, the pseudo-second order best described the adsorption kinetics of the system. Different indicators were used to determine the efficiency and accuracy of the (BP-ANN) model which are (MSE), (RMSE), (RRMSE), (MAPE). Moreover, the (FB-ANN) adequacy was checked by coefficient of correlation R^2 which found to be 0.9968. By conducting a comparative study for the experimental and the predicted results, it was found that the (FB-ANN) model was able to predict the adsorption capacity of arsenic removal satisfactorily.

Keywords: Carbon nanotubes; Deep eutectic solvents; Water treatment; Arsenicions; Neural network; Feed forward

1. Introduction

Arsenic is one of the extensively distributed metals in nature in water, soil and air. The water pollution arises due to the change of the environmental condition and industrial activities, that brings significant consideration of specialists on its remediation skills. An earlier study demonstrates that ten millions of individuals are comprehensively exposed to poisonous substantial metals per day [1]. Arsenic is one of the most poisonous heavy metals and its availability in water makes the water not desirable for drinking. The accumulation of arsenic can affect the human health such as kidney, blood cell, lesion of skin, lung, brain, stomach and even cancer [2–4]. Therefore, the world health organization (WHO) determined the maximum allowable arsenic amount at the drinking water is 0.01 mg/l [5]. Different techniques have been used for the removal of arsenic from water such as ion exchange [6], oxidation-precipitation [7], coagulation and filtration [8] and adsorption [9]. However, the performance of these techniques are not sufficient enough, therefore the need for a new method is vitally important. Nevertheless, the adsorption method gained a high interest and considered as one of the most appropriate methods due to the abil-

*Corresponding author.

ity of removing a small amount of heavy metals from a large amount of water solution. The effectiveness of adsorption is majorly dependent on the selection of appropriate process condition, including the mass of sorbent, pH, system temperature and the process duration [10]. Several studies have been done by using different type of materials to remove the arsenic ions from water for example, clay minerals [11], activated carbon [12] and biomaterials [13]. However, the use of traditional adsorbents have a drawbacks such as small adsorption capacity and low adsorption efficiency [14]. Consequently, the need for the high efficient adsorbents is necessary to remove the arsenic ions from water solution. Therefore, researchers work on finding a new promising material. Carbon nanotubes (CNTs) have different properties which make it convenient to several applications in electronics, optics, water treatment, nanotechnology and some of material science fields [15]. The nanoparticle is used as the most effectual adsorbent material for the removal of several pollutants, due to their special features such as, catalytic potential, large surface area, small size and high reactivity [16]. The most and effective material used in the water treatment field is carbon nanotubes (CNTs) for the removal of several types of pollutants [17,18]. However, there are some limitations in the CNTs application due to various flaws in solubility, difficulty in manipulation, and aggregation. In contrast, CNTs have a great property by interaction with other compounds and have a greater interaction after surface functionalization [19].

The oxidative functionalization of CNTs surface can increase the surface charge of CNTs, and this need to use a strong acid which is environmentally harmful. Therefore, finding a new kind and environmentally friendly material is crucial for the new application development [20,21].

The deep eutectic solvents (DESs) is one of the ionic liquid analogues which is presented by Abbot et al. in 2003 [22] as a cheaper replacement for developed ionic liquids (ILs). Generally, DESs made up from two or more compounds. Deep eutectic solvents (DESs) are identified as liquid combination formed by the complexation of hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD) [23,24]. The malting point of the mixed compounds are lesser than the individual compound [23]. In contrast, DES has several advantages comparing to the conventional ILs such as, diversity of physical properties and different molar ratios, easy to synthesis and cheaper price of compounds. Recently, DESs were reported in many applications; examples of such are the uses of ChCL-based DES as a functional additive for starch-based plastics [25], the synthesis of zeolite analogues [26], mediums for the deposition of specific metals in electro and electroless plating of metals [27,28]. And most recently, in nanotechnology applications [29].

The adsorption process is complicated due to many variables involved which can affect the adsorption efficiency. The conventional linear method for modelling of this kinds of processes is difficult, artificial neural network (ANN) techniques is the alternative for mapping the nonlinear relationship between variables and output professionally, can identify and reproduce non-linear relationship between inputs during training procedure in various input-output schemes [30]. Recently, ANNs technique are used for various engineering applications. ANNs consist of a massive parallel architecture which can solve the complicated problems by the assistance of highly connected neurons organised in layers. ANN considered as a powerful tool in identifying the relationships between the parameters specially at the non-linear and complex relationships. Experiments have been successfully performed to use ANN to model the adsorption of arsenic [30–32].

1.1. Problem Statement

The use of the conventional ionic liquids (ILs) is considered as environmentally harmful due to the use of strong acids and higher cost comparing to the deep eutectic solvent (DES). The use of DES has many advantages over ILs such as the diversity of physical properties and easy to synthesis. In general, the adsorption process is complicated due to the effect of many variables involved in the process, due to that the use of ANN techniques can recognize the relationship between variables such as adsorbent dosage, concentration of the heavy metals, pH and contact time. Artificial intelligence (AI) process is powerful technique that has been used successfully for the engineering applications since decreases the required time and cost for the experimental work. The advantages of the modeling techniques are formulating the knowledge, describing the process and extending the experimental results.

1.2. Objective

One hydrogen bond donor (HBD) which is glycerol (Gly) and one type of phosphonium based salts are used which is methyltriphennylos phosphonium bromide (MTPB) to prepare the DES, the salts is mixed with (Gly) to produce the DESs. Therefore, the CNTs were pre-oxidized with $KMnO_4$ and subsequently functionalized by the synthesized DESs. The functionalized CNTs are used to remove the As^{3+} from water. Four variables will be considered during the experimental work such as, adsorbent dosage, heavy metal concentration, PH and processing time.

The artificial neural network (ANN) modeling technique will be used in this study to create an ANN model to establish the relationship that exists between the variables, and to predict the adsorption capacity of the DES-CNTs forAs^{3+} removal from water solution based on the experimental data set prepared in the lab scale.

2. Experimental and methodology

2.1. Chemicals and materials

The materials used in the experimental work are multiwall carbon nanotube (MWCNTs) with specification of D 6–9 nm × L5 μm, >95% carbon, potassium permanganate ($KMnO_4$), Gly, hydrochloric acid (36.5–38%), and sodium hydroxide pellets were all provided by SIGMAALDRICH. The arsenic standard solution of 1000 mg/L and MTPB with >99% purity were provided by Merck, Germany.

2.2. Synthesis of DESs

The synthesising of DES was the result of stirring a mixture of Gly and MTPB at molar ratio of 3:1 HBD: salt at 400

rpm and temperature of 80ºC. The mixing time was 3 h until the DES turn into homogenous mixture without precipitation [33]. The produced DES will be referred as (m) in this study. The prepared DES is kept in controlled environment to avoid the effect of the humidity.

2.3. Functionalization of MWCNTs by M-DES

After drying the pristine MWCNTs (P-CNTs) at 100ºC overnight. 7 ml of $KMnO_4$ was added to 200 mg of P-CNTs and sonicated for 2 h at 65ºC to produce K-CNTs [34]. The functionalization by m-DES was conducted by mixing 200 mg of K-CNTs with 7 ml of m-DES under sonication for 3 h at 65ºC to produced mK-CNTs. Later, a filtration process was performed by washing the functionalized CNT using distilled water and filtered by PTFE 0.45 µm membrane until the pH of the filtered water reached neutral.

2.4. Characterization of functionalized CNTs

The characterization of the P-CNTs, K-CNTs and mK-CNTs adsorbent was done by using Fourier transform infrared (FTIR) to recognize the surface modification. The Raman spectroscopy also used to find the Raman shift spectra to recognize the degree of functionalization. The zeta potential also used to study the partials surface charge.

2.5 Adsorption experiments

The prepared mK-CNTs adsorbent was used in this study to remove the As^{3+} from water. Batch adsorption study was conducted using various amount of adsorbent (20, 30 and 40 mg), arsenic concentration (1, 3 and 5 mg/L) and different values of pH (3, 5 and 8). A 50 ml of contaminated water in a 250-ml flask, the flasks were shaking at 180 rpm using a mechanical system at room temperature. The number of samples prepared in this study is 213. The concentrations of arsenic were tested at different time to study the equilibrium time of adsorption.

3. Back propagation neural network (BPNN)

Recently, a significant improvement in the artificial neural network (ANN) techniques use in different fields for the prediction of difficult and complicated systems. ANN system able to improve the predicting ability of models at time the statistical and mathematical procedure are complicated to predict and formulate with anticipated accuracy. In this study, the sorption efficiency estimation by using analytical and mathematical tools is complicated due to the complexity and non-linear relationship between the variable of arsenic (III) removal. Consequently, in this study the ANN techniques have been used for prediction reason due to the high ability of ANN to perceive the input and output professionally in the complicated situation.

The back propagation neural network (BP-NN) structure containing of three different layers such as input layer which receive the inputs from the source, hidden layer which process the received signals from the input layer and output layer which deliver the results have been predicted in this study, the structure of the feed-forward back-propagation presented in Fig.1. There are two stages

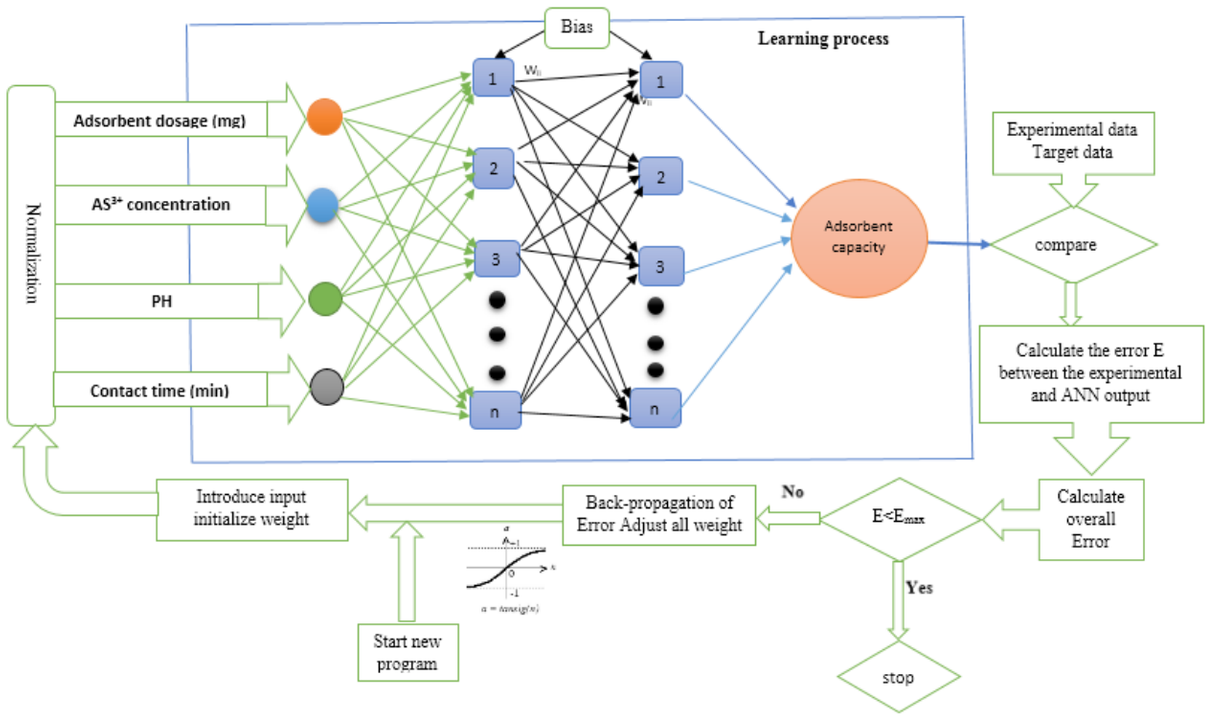

Fig. 1. Feed-forward back-propagation neural network structure.

in the neural network functioning the first stage is training and the second stage is testing. The structure of the network can be presented as B-R-N, the input layer presented by B which is identified by the number of input variables. Whereby, the hidden neuron of hidden layer is presented by R, the number of output layer neuron is presented by N the number of the output layer neuron is depending on the number of desired output. An output sources deliver information to input layer, the inputs number depending on the output sources variable, the input layer sends the information to the hidden layer and do all the processing on the information and send them to the output layer, the output layer creates the result and send it to an external receptor. The interaction between the layers is called as weight (W_{ii}) the weight factor can modify the values of the transferred signals, the sigmoid transfer function (f) also modify the total of the information. In the same way, the output layer signals also modified by the weight factor (W_{ii}) of the k_{th} layer. All the modified information by sigmoid transfer function (f) are combined at the output layer [35].

Let $I_s = (I_{s1}, I_{s2}, Is_{3,\ldots} I_{sI})$, S = 1,2,3,…,N is S_{th} manner among N input manner, where W_{kj} and W_{ji} are the connection weight between j_{th} hidden neuron to i_{th} input neuron, and k_{th} output neuron to j_{th} hidden neuron, respectively.

The output neuron form of the input layer is:

$$D_{si} = I_{si} \quad i = 1,2,3,\ldots,B \tag{1}$$

$$D = f\left(\sum_{i=1}^{I} w_{ji} D_{si}\right), \; i = 1, 2, 3, \ldots, R \tag{2}$$

The output layer neuron is:

$$D_{sk} = f\left(\sum_{j=0}^{R} w_{kj} D_{sj}\right), \; k = 1, 2, 3, \ldots, N \tag{3}$$

There are plenty of Feed-forward Back-propagation Neural Network (FBNN) transfer function in the back propagation unit. The following transfer function selected principles used as a monotonous non-decreasing, differentiable and continuous function. In this work, the most universal binary logistic sigmoid transfer function is used and it is written as following:

$$f(x) = \frac{1}{1 + e^{-x}} \tag{4}$$

The concentration of metals, adsorbent dosage, pH, and contact time are the input variables used in the ANN model are shown in Table 1.

Table 1
The range of input and output parameters

Parameters	Minimum	Maximum
Adsorbent dosage (mg)	20	40
Initial concentration of As^{3+} (mg/L)	1	5
pH	3	8
Contact time (min)	1	310
Uptake capacity (mg/g) (output)	0	3.82

The efficiency of adsorbent is the desired from the output of the network. Two hundred and thirteen experimental data are prepared in lab scale and used for the modeling. The used data are separated into two sets training set and testing set, (88%) of the data are used for the training and (12%) are used for the testing. There are two types of learning methods, the supervised and unsupervised methods, in this study the supervised technique has been used.

The predicted results are compared with the experimental used data by using the mean square error to calculate the occurred error between the predicted data and the desired data. The maximum value of mean square error limited based on the user desire, if the value is not in the limit prescribed, then its back propagation the output to the input, and the weight is adjusted until the iteration number meet the prescribed limit. The mean square error E_s is defined as:

$$E_s = \sum_{i=1}^{n} \frac{1}{2} \left(Q_{si} - D_{si}\right)^2 \tag{5}$$

where Q_{si} is the desired value, and D_{si} is the is the predicted output.

The mean square error value is supervised at the training stage. At the initial training phase, the value of the error is usually decreased, the training error start to rise when the overfitting start to happen. The training stop when the error of training begins to increase and the minimum value of weight at training are returned.

3.1. Model evaluation indicators

Different indicators will be used to evaluate the ANN model, by using the actual and predicted results, to examine the accuracy of ANN model. The behaviour of ANN model carried out by employing various indicators such as the relative root mean square error (RRMSE), mean square error (MSE), root mean square error (RMSE), mean absolute percentage error (MAPE) and relative error (RE). The formulas of the maintained indicators are as follows:

$$RRMSE = \left[\frac{1}{n}\sum_{t=1}^{n}\left(\frac{D_{a(t)} - D_{f(t)}}{D_{a(t)}}\right)^2\right]^{\frac{1}{2}} \tag{6}$$

$$MSE = \frac{1}{n}\sum_{i=1}^{n}\left(D_{a(t)} - D_{f(t)}\right)^2 \tag{7}$$

$$RMSE = \left[\frac{1}{n}\sum_{t=1}^{n}\left(D_{a(t)} - D_{f(t)}\right)^2\right]^{\frac{1}{2}} \tag{8}$$

$$MAPE = \frac{1}{n}\sum_{t=1}^{n}\left|\frac{\left(D_{a(t)} - D_{f(t)}\right)}{D_{a(t)}}\right| \times 100 \tag{9}$$

$$RE = \frac{D_{a(t)} - D_{f(t)}}{D_{a(t)}} \times 100 \tag{10}$$

where $D_{f(t)}$ = the simulated value; $D_{a(t)}$ = the actual value.

Generally, RRMSE, MSE, RMSE, MAPE and RE indicators were selected to evaluate the performance of models, all

the indicators are based on the obtained result by comparing the evaluated error of the actual and simulated results. The model with smallest error considered as the best model.

4. Result and dissection

4.1. Hybrid material characterization

The Raman spectroscopy has the capability to indicate the functionalization degree for the Carbon materials, by comparing the intensity of *D* band (I_D) with the *G* band (I_G), I_D/I_G [36]. In this work, the I_D/I_G for the P-CNTs found 1.11, by adding the $KMNO_4$ the I_D/I_G ratio reached to 1.16. Afterward, with functionalization by m-DES, the surface deformation of CNTs has been increased by bring in a new functional group in sp3 directions, resulting in the development of the I_D/I_G ratio of the mK-CNTs to 1.22. These results were in agreement with the FT-IR analysis where the functionalization with $KMnO_4$ increased the hydrophilicity of the CNTs surface by introducing O-H functional groups. By contrast, the m-DES increased the hydrophilicity of the surface where the O-H presence was completely disappeared. In addition, the PO^{-3} presence at wave number range of 450–500 cm^{-1}. The absolute zeta potential was increased significantly after the functionalization m-DES where its reached 39.78 mV. It is well known that the surface area of an adsorbent is of high influence on the adsorption efficiency, herein the surface area was increased after each functionalization step. The surface area of P-CNTs, K-CNTs, mK-CNTs was 123.5, 158.9 and 205.5 respectively [37].

4.2. Influence of pH

The pH of solution is a function of the arsenic ions removal, in order to study the pH influence, the pH values were varied in this study in the range of 3.0–8.0 with fixing all the involved parameters in the experimental work. Two initial concentrations of arsenic 1 mg/L and 3 mg/L were used in order to examine the effect of pH with different initial concentration. The relationship between the pH and the adsorption efficiency can be clarified by the mechanism of the electrostatic attraction between the arsenic species and the negative charged adsorbents. The adsorbents are highly protonated at lower pH value thus, will result in a high attraction electrostatic, which lead to a higher attraction between the negatively adsorbent charged and anion resulting in a higher adsorption capacity. Whereby, at higher value of pH the adsorbent capacity is decreasing. The process might happen due to, the ionization of adsorbent acidic or repulsive force might happen between the arsenic ions and the adsorbent negatively charged. The ANN technique is used for the modeling and prediction of the obtained data from the experimental work, the prediction results shows a good agreement with the experimental result trend. The ANN outputs and the experimental results as the function of pH versus the uptake capacity are presented in Fig. 2 A, B.

4.3. Effect of adsorbent dosage

Adsorbent dose is one of the important factors involved in the adsorption process, the adsorbent dose effect on the

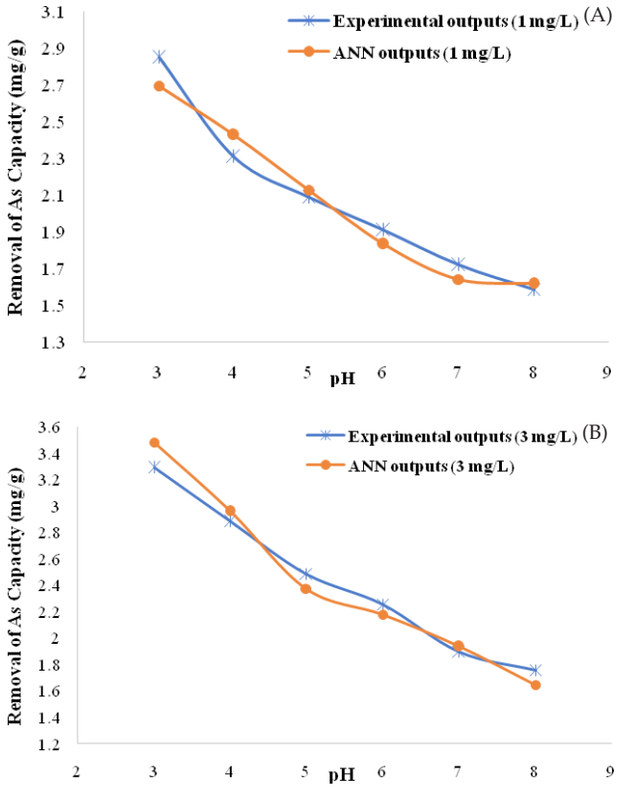

Fig. 2. ANN and experimental outputs as pH function (a) at 1 mg/L initial concentration, (b) at 3 mg/L initial concentration.

As^{3+} removal is examined at pH 5.0, with 1 mg/L and 3 mg/L As^{3+} initial concentration by keeping the other involved factors as constant. The As^{3+} removal capacity is decreased from 2.164 mg/m to 1.883 mg/g by increasing the adsorbent dosage from 20 mg to 30 mg and 1.883 mg/g to 1.761 mg/g by increasing the adsorbent dosage from 30 mg to 40 mg at initial concentration of 3 mg/L. While at initial concentration of 1 mg/L, the uptake capacity decreased from 2.164 mg/g to 1.315 mg/g with increasing the adsorbent dosage from 20 mg to 30 mg, whereby, increasing the adsorbent dosage from 30 mg to 40 mg the uptake capacity decreased from 1.315 mg/g to 1.264 mg/g. The decreasing in the uptake capacity with increasing in the adsorbent dosage might be attributed with increasing the adsorbent surface area following in an increase of more active sites [38,39]. The obtained data from the experimental work are trained and predicted by using the ANN modeling techniques. The ANN model prediction found satisfactory for the experimental data observation. The experimental and predicted output of the ANN are presented in Fig. 3 A, B.

4.4. Effect of initial concentration

The effect of the initial concentration on the adsorption capacity is studied by varying the arsenic initial concentration from (1–5 mg/l), the initial concentration effect studied at 3 and 5 pH, all the other involved parameters are fixed, contact time 120 min and adsorbent dosage 30 mg. At pH 3,

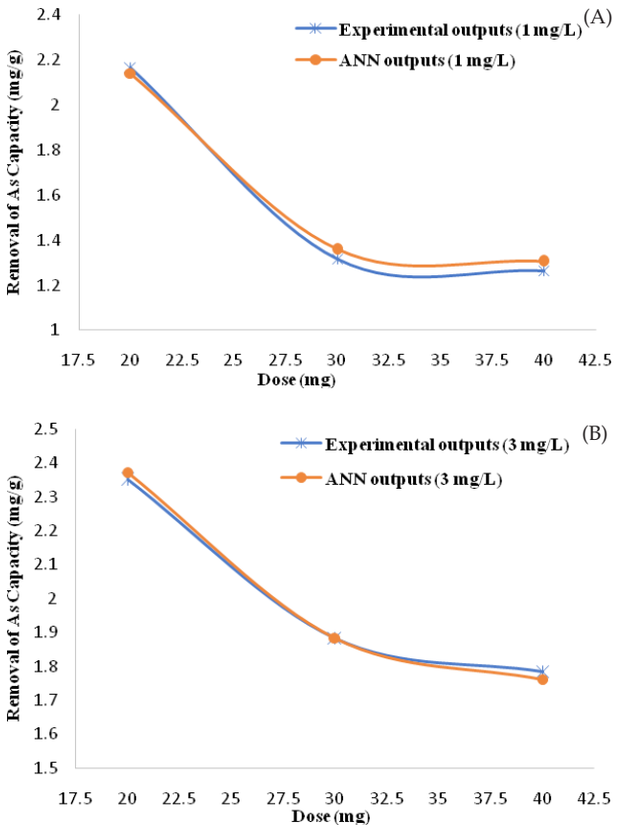

Fig. 3. Experimental and ANN output as the function of adsorbent dosage (a) at 1 mg/L initial concentration, (b) at 3 mg/L initial concentration.

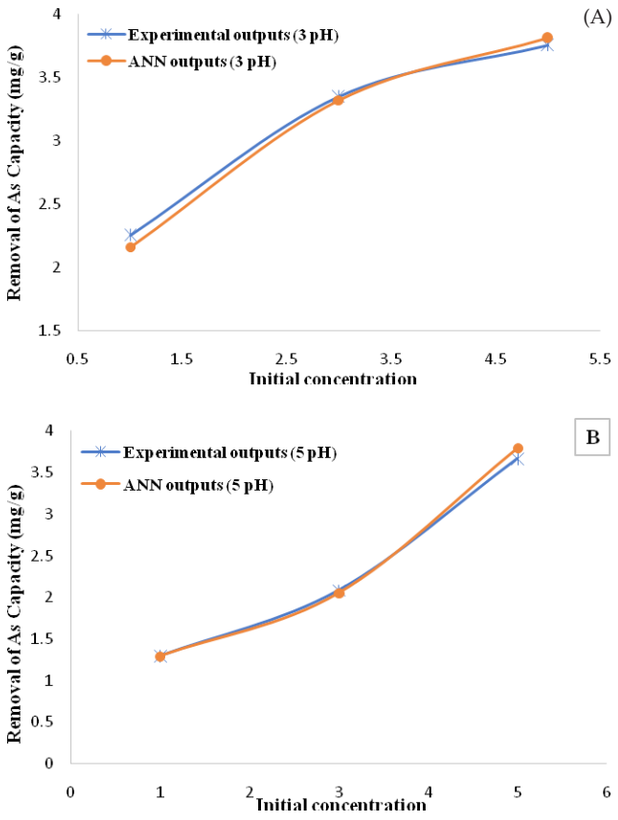

Fig. 4. Experimental and ANN output as the function of initial concentration (a) at pH 3 (b) at pH 5.

the initial arsenic concentration increased from 1 to 3 mg/l and the uptake capacity increased from 1.29 to 2.08 mg/g respectively, whereas, with increasing the initial concentration from 3 to 5 mg/l the uptake capacity increased from 2.08 to 3.66 mg/g. Whereby, at pH 5, there uptake capacity increases from 2.25 to 3.35 mg/g when increasing the initial concentration from 1 to 3 mg/g respectively. While, with increasing the initial concentration from 3 to 5 mg/l the uptake capacity increased from 3.35 to 3.75 mg/g respectively. This might be attributed due to the increase in the driving force of the mass transfer which led to an increase in the uptake capacity of As^{3+} ions from water solution. At low concentration, the As^{3+} ions interact at the adsorbent active site whereas, at higher As^{3+} concentration, the adsorbent active site will be saturated and the removal percentage will be lower [40]. The obtained data from the experimental work are trained and predicted by using the ANN modeling techniques. The ANN model prediction found satisfactory for the experimental data observation. The experimental and predicted output of the ANN are presented in Fig. 4 a, b.

4.5. Adsorption kinetics study

The adsorption kinetic study is an important study as it gives a significant information about the mechanism and pathway of the adsorption reactions, also can provide an information about the solute removal rate [41]. In this work, three kinetic models were used namely pseudo-first-order, pseudo-second-order and intraparticle diffusion model to investigate the mechanism and rate of the adsorption process. The kinetic study performed with 1 mg/L initial concentration, 30 mg adsorbent dosage and 180 rpm agitation speed, with, 5 and 8 pH. The equilibrium time of the experiment was after 240 min. The coefficients of correlation (R^2) values were used as the conformity indicator between the experiment and the predicted by each kinetic model.

The ANN technique is used for the modeling and prediction of the obtained data from the experimental work, the three kinetics models used for the experimental data also applied on the ANN outputs. The pseudo-second order describe the adsorption kinetics of this study comparing to the intraparticle diffusion and pseudo-first order models. The pseudo-second order R^2 at pH 5 is 0.9972 for the experiment data and 0.9973 for the ANN outputs whereby, for pH 8 the R^2 of the pseudo-second order was 0.9939 for the experimental data and 0.9962 for the ANN outputs the R^2 for all the three kinetics models used are summarised in Table 2. The ANN model shows a good agreement with the experimental work, the experiment and ANN results are presented in Fig. 5.

4.6. Arsenic removal prediction

The artificial neural network back-propagation (ANN-BP) was used for the prediction of arsenic removal

Table 2
Adsorption kinetics and correlation coefficient

PH	C_0 mg/L	Pseudo-first-order $\ln(q_e - q_t)$ vs time (t)		Pseudo-second-order (t/q_t vs t)		Intraparticle (q_t vs $t^{0.5}$)	
		Experimental R^2	ANN outputR^2	Experimental R^2	ANN output R^2	Experimental R^2	ANN output R^2
5	1	0.831	0.8225	0.9972	0.9973	0.901	0.919
8	1	0.919	0.926	0.9917	0.9904	0.89	0.8731

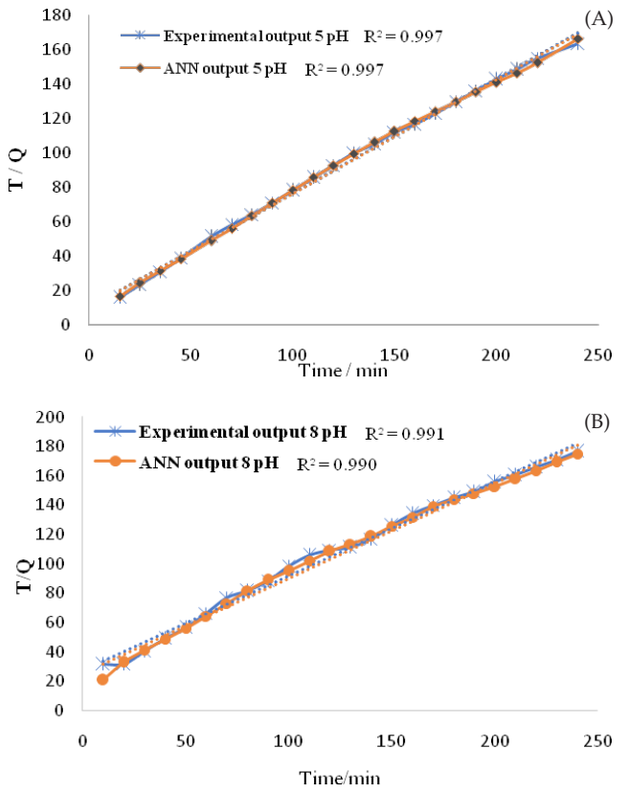

Fig. 5. Experimental and ANN output pseudo-second-order adsorption kinetics at different pH value.

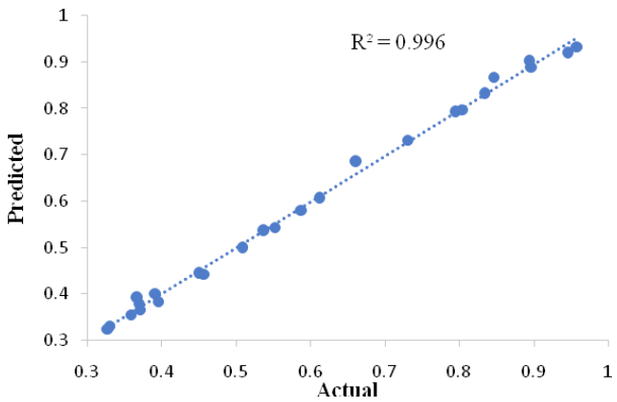

Fig. 6. Correlation coefficient of actual and predicted arsenic removal (testing data).

Table 3
Evaluation indicators

Evaluation indicators	FFNN
MSE	$1.54\ 10^{-4}$
RMSE	$1.24\ 10^{-2}$
RRMSE	$2.16\ 10^{-2}$
MAPE	1.71

efficiency by using the functionalized carbon nanotube (CNTs) material. The parameters used in this study are arsenic concentration (1 mg/l, 3 mg/l and 5 mg/l), pH (3–8), adsorbent dosage (20–40 mg) and contact time until the equilibrium of reaction. Two hundred and thirteen (213) combinations were prepared in lab scale and divided into two sets training and testing set, one hundred eighty-eight (188) data were used for the training and twenty-five (25) data were used for the testing. The MATLAB R2014a programme was used in this study. The optimum hidden layers used for the model creation are two hidden layers with 10 neurons in each hidden layer with one input layer and one output layer. The (trainbr) was selected to update the bias and weight value correspond to the momentum and the tangent sigmoid transfer function (tansig) was selected as transfer function for the network. The nodes number at the hidden layer were selected by training and testing the network with different neuron number and checking the value of the mean square error (MSE) of the testing set. The network performance is depending on the net input, weight of (trainbr) and tangent sigmoid transfer function (tansig). The minimum value of mean square error (MSE) achieved is ($1.54\ 10^{-4}$) at the testing phase, with correlation coefficient (R^2) of (0.9968), which shows a good agreement between the actual and the predicted data, the correlation coefficient plot for the testing set is presented in Fig. 6. Different indicators were used to evaluate the created model such as relative root mean square error (RRMSE), root mean square error (RMSE), mean square error (MSE) and mean absolute percentage error (MAPE), the results of all the used indicators are presented in Table 3.The relative error is one of the error indicators in the modeling prediction it compares the actual values to predicted values Fig. 7 shows the relative error percentage of the model, the maximum error value for the FFNN model is 5.97%. The best prediction performance is depending on the neural network training. This study is meant to get the mathematical approach benefit at the real-time experiment. The ANN model`s development is becom-

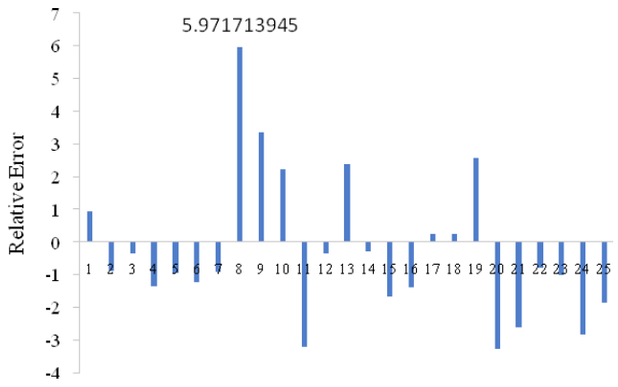

Fig. 7. Illustrates the accuracy of the hybrid model on the testing data.

ing the issues and challenges of the real-time experiment. This work currently under development phase to obtain a better feedback from the neural network in the hazardous ions removal.

5. Conclusion

In this work, a novel adsorbent was developed by using two DESs systems for the CNTs functionalization. The adsorbent was characterized by using zeta potential, Raman spectroscopy and FTIR. The adsorbent surface area increased after the functionalization by mK-CNTs. The experimental work has been carried out for the removal of arsenic from water solution. The new adsorbent found as an effective material for arsenic removal from water. Three kinetics models were used in this study which are Pseudo-first-order, Pseudo-second-order and the Intraparticle with different values of pH, the pseudo-second order describe the adsorption kinetics of this study. The ANN technique was used successfully for the prediction of arsenic removal from water by using m-DES functionalized-CNTs (mK-CNTs). A three layers' neural network designed for the prediction of arsenic removal capacity from water, the feed-forward back-propagation algorithm was used in this study. Various indicators were used to evaluate the accuracy of ANN model such as (RRMSE, MSE, RMSE, MAPE and RE). The ANN output showed a good agreement with the experimental data, the best correlation coefficient R^2 is (0.9968) at the testing phase. This study conclude that the ANN system is able to predict the adsorption capacity of arsenic from water.

Acknowlgment

The authors express their thanks to the University of Malaya for funding this research. UMRG (RP017A-13AET)

References

[1] D. Briggs, Environmental pollution and the global burden of disease, British Med. Bull., 68 (2003) 1–24.
[2] Z. Cheng, F. Fu, D.D. Dionysiou, B. Tang, Adsorption, oxidation, and reduction behavior of arsenic in the removal of aqueous As (III) by mesoporous Fe/Al bimetallic particles, Water Res., 96 (2016) 22–31.
[3] D.Q. Hung, O. Nekrassova, R.G. Compton, Analytical methods for inorganic arsenic in water: a review, Talanta, 64 (2004) 269–277.
[4] V.K. Sharma, M. Sohn, Aquatic arsenic: toxicity, speciation, transformations, and remediation, Environ. Int., 35 (2009) 743–759.
[5] G. Liu, X. Zhang, J.W. Talley, C.R. Neal, H. Wang, Effect of NOM on arsenic adsorption by TiO_2 in simulated As (III)-contaminated raw waters, Water Res., 42 (2008) 2309–2319.
[6] B. An, Q. Liang, D. Zhao, Removal of arsenic (V) from spent ion exchange brine using a new class of starch-bridged magnetite nanoparticles, Water Res., 45 (2011) 1961–1972.
[7] S. Tresintsi, K. Simeonidis, G. Vourlias, G. Stavropoulos, M. Mitrakas, Kilogram-scale synthesis of iron oxy-hydroxides with improved arsenic removal capacity: Study of Fe (II) oxidation–precipitation parameters, Water Res., 46 (2012) 5255–5267.
[8] M.B. Baskan, A. Pala, A statistical experiment design approach for arsenic removal by coagulation process using aluminum sulfate, Desalination, 254 (2010) 42–48.
[9] J. Pattanayak, K. Mondal, S. Mathew, S. Lalvani, A parametric evaluation of the removal of As (V) and As (III) by carbon-based adsorbents, Carbon, 38 (2000) 589–596.
[10] E. Lourie, E. Gjengedal, Metal sorption by peat and algae treated peat: Kinetics and factors affecting the process, Chemosphere, 85 (2011) 759–764.
[11] J.U.K. Oubagaranadin, Z. Murthy, Isotherm modeling and batch adsorber design for the adsorption of Cu (II) on a clay containing montmorillonite, Appl. Clay Sci., 50 (2010) 409–413.
[12] J.P. Chen, S. Wu, Acid/base-treated activated carbons: characterization of functional groups and metal adsorptive properties, Langmuir, 20 (2004) 2233–2242.
[13] V. Gupta, A. Rastogi, V. Saini, N. Jain, Biosorption of copper (II) from aqueous solutions by Spirogyra species, J. Colloid Interface Sci., 296 (2006) 59–63.
[14] G.P. Rao, C. Lu, F. Su, Sorption of divalent metal ions from aqueous solution by carbon nanotubes: a review, Separ. Purif. Technol., 58 (2007) 224–231.
[15] M.A. Atieh, O.Y. Bakather, B. Al-Tawbini, A.A. Bukhari, F.A. Abuilaiwi, M.B. Fettouhi, Effect of carboxylic functional group functionalized on carbon nanotubes surface on the removal of lead from water, Bioinorg. Chem. Applic., 2010 (2011).
[16] I. Ali, New generation adsorbents for water treatment, Chem. Rev., 112 (2012) 5073–5091.
[17] A. Abbas, A.M. Al-Amer, T. Laoui, M.J. Al-Marri, M.S. Nasser, M. Khraisheh, M.A. Atieh, Heavy metal removal from aqueous solution by advanced carbon nanotubes: critical review of adsorption applications, Separ. Purif. Technol., 157 (2016) 141–161.
[18] R.K. Ibrahim, M. Hayyan, M.A. AlSaadi, A. Hayyan, S. Ibrahim, Environmental application of nanotechnology: air, soil, and water, Environ. Sci. Pollut. Res., 23 (2016) 13754–13788.
[19] E.T. Thostenson, Z. Ren, T.-W. Chou, Advances in the science and technology of carbon nanotubes and their composites: a review, Comp. Sci. Technol., 61 (2001) 1899–1912.
[20] M. Martinez, M. Callejas, A. Benito, M. Cochet, T. Seeger, A. Anson, J. Schreiber, C. Gordon, C. Marhic, O. Chauvet, Modifications of single-wall carbon nanotubes upon oxidative purification treatments, Nanotechnology, 14 (2003) 691.
[21] M. Hayyan, A. Abo-Hamad, M.A. AlSaadi, M.A. Hashim, Functionalization of graphene using deep eutectic solvents, Nanoscale Res. Lett., 10 (2015) 324.
[22] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, Novel solvent properties of choline chloride/urea mixtures, Chem. Commun., (2003) 70–71.
[23] A.P. Abbott, D. Boothby, G. Capper, D.L. Davies, R.K. Rasheed, Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids, J. Amer. Chem. Soc., 126 (2004) 9142–9147.

[24] J.T. Gorke, F. Srienc, R.J. Kazlauskas, Hydrolase-catalyzed biotransformations in deep eutectic solvents, Chem. Commun., (2008) 1235–1237.
[25] E. Leroy, P. Decaen, P. Jacquet, G. Coativy, B. Pontoire, A.-L. Reguerre, D. Lourdin, Deep eutectic solvents as functional additives for starch based plastics, Green Chem., 14 (2012) 3063–3066.
[26] E.R. Cooper, C.D. Andrews, P.S. Wheatley, P.B. Webb, P. Wormald, R.E. Morris, Ionic liquids and eutectic mixtures as solvent and template in synthesis of zeolite analogues, Nature, 430 (2004) 1012–1016.
[27] A.P. Abbott, J. Griffith, S. Nandhra, C. O'Connor, S. Postlethwaite, K.S. Ryder, E.L. Smith, Sustained electroless deposition of metallic silver from a choline chloride-based ionic liquid, Surf. Coat. Technol., 202 (2008) 2033–2039.
[28] A.P. Abbott, G. Capper, K.J. McKenzie, K.S. Ryder, Electrodeposition of zinc–tin alloys from deep eutectic solvents based on choline chloride, J. Electroanal. Chem., 599 (2007) 288–294.
[29] A. Abo-Hamad, M. Hayyan, M.A. AlSaadi, M.A. Hashim, Potential applications of deep eutectic solvents in nanotechnology, Chem. Eng. J., 273 (2015) 551–567.
[30] A. Giri, R. Patel, S. Mahapatra, Artificial neural network (ANN) approach for modelling of arsenic (III) biosorption from aqueous solution by living cells of Bacillus cereus biomass, Chem. Eng. J., 178 (2011) 15–25.
[31] K.H. Cho, S. Sthiannopkao, Y.A. Pachepsky, K.-W. Kim, J.H. Kim, Prediction of contamination potential of groundwater arsenic in Cambodia, Laos, and Thailand using artificial neural network, Water Res., 45 (2011) 5535–5544.
[32] M. Podder, C. Majumder, The use of artificial neural network for modelling of phycoremediation of toxic elements As (III) and As (V) from wastewater using Botryococcus braunii, Spectrochim. Acta Part A: Molec. Biomol. Spectrosc., 155 (2016) 130–145.
[33] M.K. AlOmar, M. Hayyan, M.A. Alsaadi, S. Akib, A. Hayyan, M.A. Hashim, Glycerol-based deep eutectic solvents: Physical properties, J. Mol. Liq., 215 (2016) 98–103.
[34] M.A. AlSaadi, A. Al Mamun, M.Z. Alam, M.K. Amosa, M.A. Atieh, Removal of cadmium from water by CNT–PAC composite: effect of functionalization, Nano, 11 (2016) 1650011.
[35] D.P. Strik, A.M. Domnanovich, L. Zani, R. Braun, P. Holubar, Prediction of trace compounds in biogas from anaerobic digestion using the MATLAB Neural Network Toolbox, Environ. Model. Software, 20 (2005) 803–810.
[36] T.J. Aitchison, M. Ginic-Markovic, J.G. Matisons, G.P. Simon, P.M. Fredericks, Purification, cutting, and sidewall functionalization of multiwalled carbon nanotubes using potassium permanganate solutions, J. Phys. Chem. C, 111 (2007) 2440–2446.
[37] M.K. AlOmar, M.A. Alsaadi, M. Hayyan, S. Akib, M.A. Hashim, Functionalization of CNTs surface with phosphonuim based deep eutectic solvents for arsenic removal from water, Appl. Surf. Sci., 389 (2016) 216–226.
[38] B. Das, N. Mondal, R. Bhaumik, P. Roy, Insight into adsorption equilibrium, kinetics and thermodynamics of lead onto alluvial soil, Int. J. Environ. Sci. Technol., 11 (2014) 1101–1114.
[39] M.S. Kumar, B. Phanikumar, Response surface modelling of Cr^{6+} adsorption from aqueous solution by neem bark powder: Box–Behnken experimental approach, Environ. Sci. Pollut. Res., 20 (2013) 1327–1343.
[40] A. Banerjee, P. Sarkar, S. Banerjee, Application of statistical design of experiments for optimization of As (V) biosorption by immobilized bacterial biomass, Ecol. Eng., 86 (2016) 13–23.
[41] S. Ayoob, A. Gupta, P. Bhakat, Performance evaluation of modified calcined bauxite in the sorptive removal of arsenic (III) from aqueous environment, Colloids Surf. A: Physicochem. Eng. Asp., 293 (2007) 247–254.